

# A Theory of Redox Catalyzed Electron Tunnelling in Electrochemical Contacts

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A theory of redox catalyzed electron tunnelling through *in situ* electrochemical tunnel contacts is presented. The process under discussion represents electron transfer from a metal electrode to the STM tip in the electrolyte solution via an electron energy level of atomic groups confined between the two metals. This is a typical situation, for example, for STM of adsorbed species (atoms, inorganic and biological molecules).

Several points are of importance for the physical mechanism of these processes:

- (1) The bridge group B may be in oxidized or reduced state
- (2) Electron state in the bridge group interacts strongly with vibrational subsystem (polar solvent or local vibrational modes)
- (3) Due to this interaction equilibrium position of the electron energy levels of oxidized,  $B_{ox}$ , and reduced,  $B_{red}$ , forms of B,  $\mathcal{M}_{ox}$  and  $\mathcal{M}_{red}$ , are located, respectively, far above and far below of the Fermi level  $\mathcal{M}_{FL}$  and  $\mathcal{M}_{FR}$  of the left (substrate) and right (STM tip) metals
- (4) Fluctuations of the configurations of vibrational subsystem bring the energy level of the bridge group into the «energy tip» region  $eV_{bias}$  for a short time
- (5) The dynamic motion in vibrational subsystem completes redox transformation of the bridge group
- (6) Two potential drops can be varied independently: bias voltage  $V_{bias}$  and electrode potential  $\mathcal{E}$  (or overpotential  $\mathcal{E}$ ).

Detailed picture of the elementary act of the redox process depends on the strength of interaction of the bridge group B with metals. Three main situations are distinguished:

- 1) Totally non-adiabatic transitions when the coupling with both metals is weak.
- 2) Partially adiabatic transitions when the coupling with one of metals is weak, whereas it is strong with the other one.
- 3) Totally adiabatic transitions when coupling with both metals is strong.

I. In the case of totally non-adiabatic transitions electron transfer from the left (negatively biased) metal to the bridge group most probably results in the reduction of this group with the relaxation to the final equilibrium configuration  $\mathcal{M}_{red}$ . Further electron transfer from B to the right (positively biased) metal is possible as a result of re-activation from this configuration. The electron transfer from B to the right metal results then in the oxidation of the bridge group with the relaxation to the initial equilibrium configuration  $\mathcal{M}_{tox}$ . This two-step cycle produces the transfer of one electron from the left metal to the right one. The expression for the electric current has then the form

$$i_{tunn.}^{non-ad.} = e \frac{\vec{k}_{o/r}^{n-ad} \vec{k}_{o/r}^{n-ad}}{\vec{k}_{o/r}^{n-ad} + \vec{k}_{o/r}^{n-ad} + \vec{k}_{o/r}^{n-ad}} \quad (1)$$

where the arrows show the direction of electron transfer in the oxidation (r/o) or reduction (o/r) step. Each rate constant is proportional here to  $\kappa p k_B T \ll 1$  where

$\mathcal{E}$  and  $\mathcal{D}$  are the electron transmission coefficient and density of electron states for the corresponding metal.

II. In the partially adiabatic case a redox equilibrium is established at the electrode the coupling with which is strong. The current is determined then by the rate of the electron exchange between the bridge group and the other electrode similar to that for ordinary electrochemical electron transfer reactions.

III. In the case of totally adiabatic transitions a new phenomenon in tunnelling appears. Due to a strong coupling with both metals multiple electron transitions from the left metal to the bridge group and further to the right metal take place in the process of passage of the electron energy level of the bridge group through the «energy tip» region. This results in the reduction of B. The re-activation from the final equilibrium configuration B. The electric current is described by the formula

$$i_{tunn.}^{ad.} = ne \frac{\vec{k}_{o/r}^{ad} \vec{k}_{r/o}^{ad}}{\vec{k}_{o/r}^{ad} + \vec{k}_{r/o}^{ad}} \quad (2)$$

where  $n \sim eV_{bias} \mathcal{E} \mathcal{D} k_B T$  is the number of electrons transferred in each oxidation and reduction step and the condition of strong coupling with the metals has the form  $\mathcal{E} \mathcal{D} k_B T \gg 1$ .

The current (2) as a function of the overpotential  $\mathcal{E}$  has a maximum in the normal region. This maximum is due to an interplay between the overpotential dependence of the rate constants and occupation of oxidized and reduced states of the bridge group.

Effects of Coulomb blockade are expected in the system with biological molecules as a bridge when the electron transfer occurs to the metal clusters.

## References

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